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(54) Title: **MEMBRANE/ELECTRODE COMPOSITE**

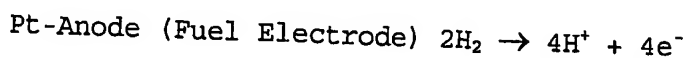
(57) Abstract: A method of manufacturing a membrane/electrode composite of a type which includes a catalyst material on a first material which comprises a first conductive polymer includes a step of contacting the first material comprising the first conductive polymer with a polar protic solvent (e.g. sulphuric acid, a sulphonic acid, hydrofluoric acid or phosphoric acid) and causing catalyst material to deposit on the first material. The composite may be used in an electrochemical device for example a fuel cell.

MEMBRANE/ELECTRODE COMPOSITE

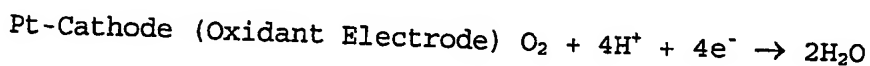
This invention relates to a membrane/electrode composite of a type which includes a catalyst material on an ion-conducting membrane and particularly, although not exclusively, relates to a method of preparing such a composite and such a composite per se.

One type of polymer electrolyte membrane fuel cell (PEMFC), shown schematically in Figure 1 of the accompanying diagrammatic drawings, may comprise a thin sheet 2 of a hydrogen-ion conducting Polymer Electrolyte Membrane (PEM) sandwiched on both sides by a layer 4 of platinum catalyst and an electrode 6. The layers 2, 4, 6 make up a Membrane Electrode Assembly (MEA) of less than 1mm thickness.

In a PEMFC, hydrogen is introduced at the anode (fuel electrode) which results in the following electrochemical reaction:



The hydrogen ions migrate through the conducting PEM to the cathode. Simultaneously, an oxidant is introduced at the cathode (oxidant electrode) where the following electrochemical reaction takes place:



Thus, electrons and protons are consumed to produce water and heat. Connecting the two electrodes through an

external circuit causes an electrical current to flow in the circuit and withdraw electrical power from the cell.

WO97/40543 describes a process for production of a  
5 cation-exchange membrane where a formulation comprising N-methylpyrrolidone (NMP) (a polar aprotic solvent), a polyaryletherketone (polyetheretherketoneketone polymer) dissolved in a solvent and a catalyst material dispersed in the solution is coated on a cation-exchange material  
10 (sulphonated polyetheretherketoneketone polymer). The coating may optionally be treated so that pores form in it. Disadvantageously, however, the polymers used to prepare the membrane have unsatisfactory properties. Furthermore, the use of NMP to cast the coating may, when  
15 in conjunction with a catalyst material, present a fire hazard.

It is an object of the invention to address problems associated with membrane/electrode composites.

20

According to a first aspect of the invention, there is provided a method of manufacturing a composite (e.g. a membrane/electrode composite) of a type which includes a catalyst material on a first material which comprises a  
25 first conductive polymer, the method including the step of contacting said first material comprising said first conductive polymer with a polar protic solvent and causing catalyst material to deposit on said first material.

30 Said first conductive polymer may comprise a thermoplastic or thermoset aromatic polymer, a polybenzazole or a polyaramid polymer, a perfluorinated ionomer, each of which has been functionalised to provide

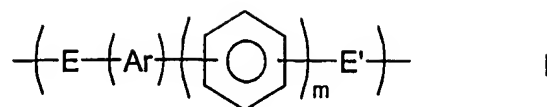
ion-exchange sites; polystyrene sulfonic acid (PSSA), polytrifluorostyrene sulfonic acid (such as those prepared from alpha, alpha, beta-trifluorostyrenes as described in US 5422411, US 5773480 and US 5834523), polyvinyl  
5 phosphonic acid (PVPA), polyvinyl carboxylic (PVCA) acid and polyvinyl sulfonic acid (PVSA) polymers, and metal salts thereof.

Examples of aromatic polymers include polysulfone  
10 (PSU), polyimide (PI), polyphenylene oxide (PPO), polyphenylene sulfoxide (PPSO), polyphenylene sulfide (PPS), polyphenylene sulfide sulfone (PPS/SO<sub>2</sub>), polyparaphenylene (PPP), polyphenylquinoxaline (PPQ), polyaryleketone and polyetherketone polymers especially  
15 polyetherketone and polyetheretherketone polymers, for example PEK™ polymers and PEEK™ polymers respectively, from Victrex Plc.

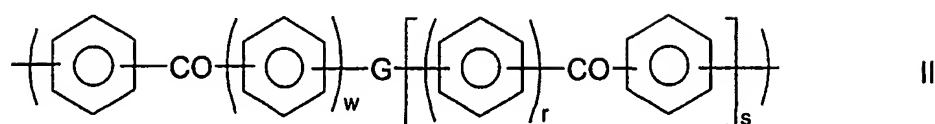
Examples of perfluorinated ionomers include carboxyl-,  
20 phosphonyl- or sulphonyl-substituted perfluorinated vinyl ethers.

Examples of one class of preferred first conductive polymers are the polymers shown in Figure 2a to 2c when  
25 functionalised to provide ion-exchange sites.

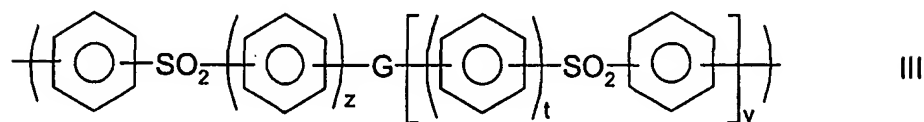
A preferred first conductive polymer is one having a moiety of formula



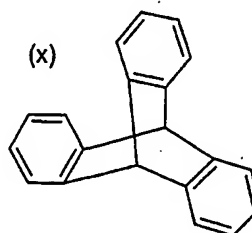
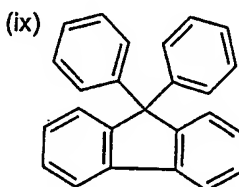
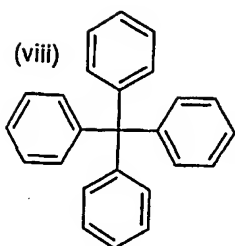
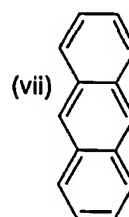
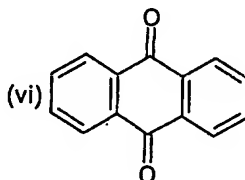
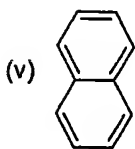
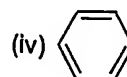
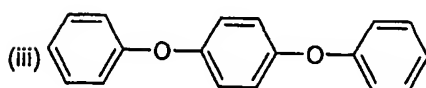
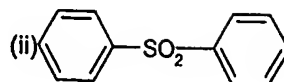
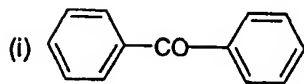
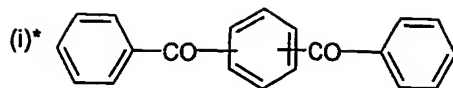
and/or a moiety of formula



5 and/or a moiety of formula



wherein at least some of the units I, II and/or III are  
 funtionalized to provide ion-exchange sites; wherein the  
 10 phenyl moieties in units I, II, and III are independently  
 optionally substituted and optionally cross-linked; and  
 wherein m, r, s, t, v, w and z independently represent zero or a  
 positive integer, E and E' independently represent an  
 oxygen or a sulphur atom or a direct link, G represents an  
 15 oxygen or sulphur atom, a direct link or a -O-Ph-O- moiety  
 where Ph represents a phenyl group and Ar is selected from  
 one of the following moieties (i)\*, (i) to (x) which is  
 bonded via one or more of its phenyl moieties to adjacent  
 moieties



In (i)\*, the middle phenyl may be 1,4- or 1,3-substituted.

Suitably, to provide said ion exchange sites, said  
 5 polymer is sulphonated, phosphorylated, carboxylated,  
 quaternary-aminoalkylated or chloromethylated, and  
 optionally further modified to yield  $-\text{CH}_2\text{PO}_3\text{H}_2$ ,  $-\text{CH}_2\text{NR}_3^{20+}$   
 where  $\text{R}^{20}$  is an alkyl, or  $-\text{CH}_2\text{NAr}_3^{x+}$  where  $\text{Ar}^x$  is an aromatic  
 (arene), to provide a cation or anion exchange membrane.  
 10 Further still, the aromatic moiety may contain a hydroxyl  
 group which can be readily elaborated by existing methods

to generate  $-\text{OSO}_3\text{H}$  and  $-\text{OPO}_3\text{H}_2$  cationic exchange sites on the polymer. Ion exchange sites of the type stated may be provided as described in WO95/08581.

5        Preferably, said first conductive polymer is sulphonated. Preferably, the only ion-exchange sites of said first conductive polymer are sites which are sulphonated.

10        References to sulphonation include a reference to substitution with a group  $-\text{SO}_3\text{M}$  wherein M stands for one or more elements selected with due consideration to ionic valencies from the following group: H,  $\text{NR}_4^{Y+}$ , in which  $\text{R}^Y$  stands for H,  $\text{C}_1\text{-C}_4$  alkyl, or an alkali or alkaline earth  
15 metal or a metal of sub-group 8, preferably H,  $\text{NR}_4^+$ , Na, K, Ca, Mg, Fe, and Pt. Preferably M represents H. Sulphonation of the type stated may be provided as described in WO96/29360.

20        Unless otherwise stated in this specification, a phenyl moiety may have 1,4- or 1,3-, especially 1,4-, linkages to moieties to which it is bonded.

25        Said first conductive polymer may include more than one different type of repeat unit of formula I; more than one different type of repeat unit of formula II; and more than one different type of repeat unit of formula III.

30        Said moieties I, II and III are suitably repeat units. In the polymer, units I, II and/or III are suitably bonded to one another - that is, with no other atoms or groups being bonded between units I, II, and III.

Where the phenyl moieties in units I, II or III are optionally substituted, they may be optionally substituted by one or more halogen, especially fluorine and chlorine, atoms or alkyl, cycloalkyl or phenyl groups. Preferred  
5 alkyl groups are  $C_{1-10}$ , especially  $C_{1-4}$ , alkyl groups. Preferred cycloalkyl groups include cyclohexyl and multicyclic groups, for example adamantyl. In some cases, the optional substituents may be used in the cross-linking of the polymer. For example, hydrocarbon optional  
10 substituents may be functionalised, for example sulphonated, to allow a cross-linking reaction to take place. Preferably, said phenyl moieties are unsubstituted.

Another group of optional substituents of the phenyl  
15 moieties in units I, II or III include alkyls, halogens,  $C_yF_{2y+1}$  where  $y$  is an integer greater than zero,  $O-R^q$  (where  $R^q$  is selected from the group consisting of alkyls, perfluoralkyls and aryls),  $CF=CF_2$ ,  $CN$ ,  $NO_2$  and  $OH$ . Trifluormethylated phenyl moieties may be preferred in some  
20 circumstances.

Where said polymer is cross-linked, it is suitably cross-linked so as to improve its properties, for example to reduce its swellability in water. Any suitable means  
25 may be used to effect cross-linking. For example, where  $E$  represents a sulphur atom, cross-linking between polymer chains may be effected via sulphur atoms on respective chains. Alternatively, said polymer may be cross-linked via sulphonamide bridges as described in US 5 561 202. A  
30 further alternative is to effect cross-linking as described in EP-A-0008895.



However, for first conductive polymers according to the inventions described herein which are crystalline (which some are) there may be no need to effect cross-linking to produce a satisfactory material. Such polymers may be easier to prepare than cross-linked polymers. Thus, said first conductive polymer of the inventions described herein may be crystalline. Preferably, said polymer is not optionally cross-linked as described.

Where  $w$  and/or  $z$  is/are greater than zero, the respective phenylene moieties may independently have 1,4- or 1,3-linkages to the other moieties in the repeat units of formulae II and/or III. Preferably, said phenylene moieties have 1,4- linkages.

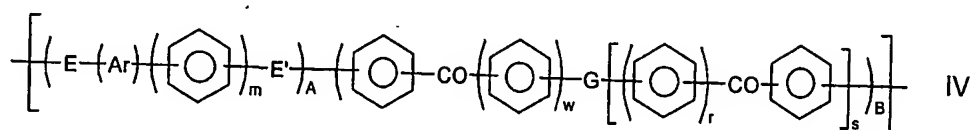
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Preferably, the polymeric chain of the polymer does not include a -S- moiety. Preferably, G represents a direct link.

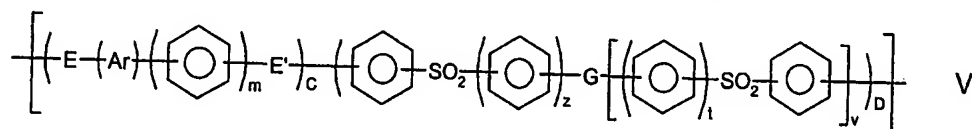
Suitably, "a" represents the mole % of units of formula I in said polymer, suitably wherein each unit I is the same; "b" represents the mole % of units of formula II in said polymer, suitably wherein each unit II is the same; and "c" represents the mole % of units of formula III in said polymer, suitably wherein each unit III is the same. Preferably, a is in the range 45-100, more preferably in the range 45-55, especially in the range 48-52. Preferably, the sum of b and c is in the range 0-55, more preferably in the range 45-55, especially in the range 48-52. Preferably, the ratio of a to the sum of b and c is in the range 0.9 to 1.1 and, more preferably, is about 1. Suitably, the sum of a, b and c is at least 90, preferably at least 95, more preferably at least 99, especially about

100. Preferably, said polymer consists essentially of moieties I, II and/or III.

Said polymer may be a homopolymer having a repeat unit  
5 of general formula



or a homopolymer having a repeat unit of general formula

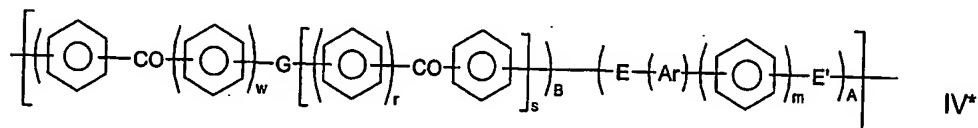


10 or a random or block copolymer of at least two different units of IV and/or V

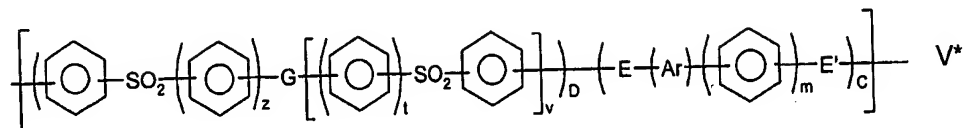
wherein A, B, C and D independently represent 0 or 1 and E, E', G, Ar, m, r, s, t, v, w and z are as described in any  
15 statement herein.

As an alternative to a polymer comprising units IV and/or V discussed above, said polymer may be a homopolymer having a repeat unit of general formula

20



or a homopolymer having a repeat unit of general formula

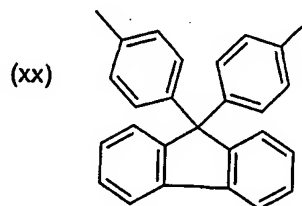
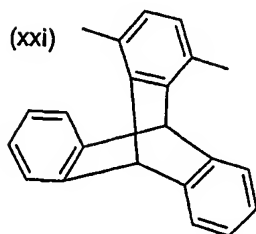
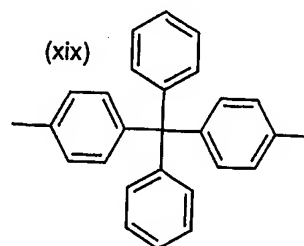
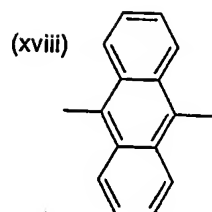
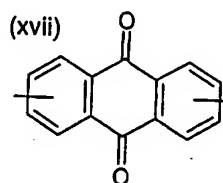
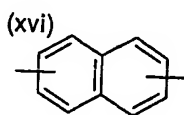
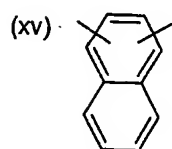
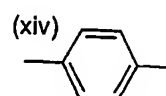
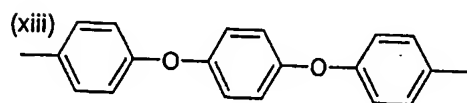
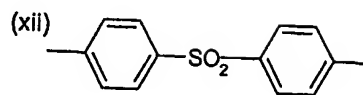
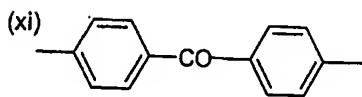
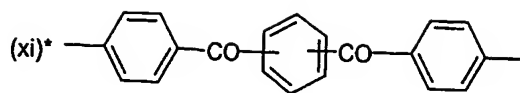


or a random or block copolymer of at least two  
 5 different units of IV\* and/or V\*, wherein A, B, C, and D  
 independently represent 0 or 1 and E, E', G, Ar, m, r, s,  
 t, v, w and z are as described in any statement herein.

Preferably, m is in the range 0-3, more preferably 0-2,  
 10 especially 0-1. Preferably, r is in the range 0-3, more  
 preferably 0-2, especially 0-1. Preferably t is in the  
 range 0-3, more preferably 0-2, especially 0-1.  
 Preferably, s is 0 or 1. Preferably v is 0 or 1.  
 Preferably, w is 0 or 1. Preferably z is 0 or 1.

15

Preferably Ar is selected from the following moieties  
 (xi)\*, (xi) to (xxi):



In (xi)\*, the middle phenyl may be 1,4- or 1,3-substituted.

Preferably, (xv) is selected from a 1,2-, 1,3-, or a 1,5- moiety; (xvi) is selected from a 1,6-, 2,3-, 2,6- or a 2,7- moiety; and (xvii) is selected from a 1,2-, 1,4-, 1,5-, 1,8- or a 2,6- moiety.

5

One preferred class of first conductive polymers may include at least some ketone moieties in the polymeric chain. In such a preferred class, the polymer preferably does not only include -O- and -SO<sub>2</sub>- moieties between aryl  
10 (or other unsaturated) moieties in the polymeric chain. Thus, in this case, suitably, a polymer of the first and/or second aspects does not consist only of moieties of formula III, but also includes moieties of formula I and/or II.

15 One preferred class of polymers does not include any moieties of formula III, but suitably only includes moieties of formulae I and/or II. Where said polymer is a homopolymer or random or block copolymer as described, said homopolymer or copolymer suitably includes a repeat unit of  
20 general formula IV. Such a polymer may, in some embodiments, not include any repeat unit of general formula V.

Suitable moieties Ar are moieties (i)\*, (i), (ii), (iv)  
25 and (v) and, of these, moieties (i), (ii) and (iv) are preferred. Preferred moieties Ar are moieties (xi)\*, (xi), (xii), (xiv), (xv) and (xvi) and, of these, moieties (xi)\*, (xi), (xii) and (xiv) are especially preferred. Another preferred moiety is moiety (v), especially, moiety (xvi).  
30 In relation, in particular to the alternative polymers comprising units IV\* and/or V\*, preferred Ar moieties are (v) and, especially, (xvi).

Preferred first conductive polymers include an electron-rich, relatively non-deactivated, easily sulphonatable unit, for example a multi-phenylene moiety or a fused-rings aromatic moiety, such as naphthalene. Such an easy to sulphonate unit may be sulphonated under relatively mild conditions to introduce two sulphonate groups per unit. Thus, preferred polymers may have at least  $10\pi$  electrons in a delocalized aromatic moiety. The number of  $\pi$  electrons may be 12 or less. Preferred polymers include a biphenylene moiety. Other preferred polymers include a naphthalene moiety. Preferred polymers include said electron rich, non-deactivated, easily sulphonatable unit bonded to two oxygen atoms. Especially preferred polymers include a -O-biphenylene-O- moiety. Other especially preferred polymers include a -O-naphthalene-O- moiety.

Preferred polymers include a first type of moiety which is relatively difficult to sulphonate and a second type of moiety which is relatively easy to sulphonate. For example, said second moiety may be sulphonatable using the relatively mild method described in Example 3 hereinafter, whereas the first moiety may be substantially non-sulphonatable in such a method. The use of the method of Example 3 may be advantageous over currently used methods which use oleum. A preferred second said moiety includes a moiety  $-\text{Ph}_n-$  wherein  $n$  is an integer of at least 2. Said moiety is preferably bound to at least one ether oxygen. Especially preferred is the case wherein said moiety is -O- $\text{Ph}_n$ -O- where said ether groups are para to the Ph-Ph bond.

30

Preferred polymers are copolymers comprising, preferably consisting essentially of, a first repeat unit which is selected from the following:

(a) a unit of formula IV wherein E and E' represent oxygen atoms, G represents a direct link, Ar represents a moiety of structure (iv), m and s represent zero, w represents 1 and A and B represent 1;

5

(b) a unit of formula IV wherein E represents an oxygen atom, E' represents a direct link, Ar represents a moiety of structure (i), m represents zero, A represents 1, B represents zero;

10

(c) a unit of formula V wherein E and E' represent oxygen atoms, G represents a direct link, Ar represents a moiety of structure (iv), m and v represent zero, z represents 1 and C and D represent 1;

15

(d) a unit of formula V wherein E represents an oxygen atom, E' represents a direct link, Ar represents a moiety of structure (ii), m represents 0, C represents 1, D represents 0; or

20

(e) a unit of formula V wherein E and E' represents an oxygen atom, Ar represents a structure (i), m represents 0, C represents 1, Z represents 1, G represents a direct link, v represents 0 and D represents 1;

25

Other preferred first repeat units include:

(aa) a unit of formula IV wherein E represents an oxygen atom, E' represents a direct link, Ar represents a  
30 structure (i)\*, m represents 0, A represents 1, B represents 0;

(bb) a unit of formula IV wherein E and E' represent oxygen atoms, Ar represents a structure (iv), m and w represent 0, G represents a direct link, s and r represent 1, A and B represent 1;

5

(cc) a unit of formula IV wherein E and E' represent oxygen atoms, Ar represents a structure (i), m and w represent 0, G represents a direct link, s and r represent 1, A and B represent 1;

10

and a second repeat unit which is selected from the following:

(f) a unit of formula IV wherein E and E' represent oxygen atoms, G represents a direct link, Ar represents a moiety of structure (iv), m represents 1, w represents 1, s represents zero, A and B represent 1;

(g) a unit of formula IV wherein E represents an oxygen atom, E' is a direct link, G represents a direct link, Ar represents a moiety of structure (iv), m and s represent zero, w represent 1, A and B represent 1;

(h) a unit of formula V wherein E and E' represent oxygen atoms, G represents a direct link, Ar represents a moiety of structure (iv), m represents 1, z represents 1, v represents 0, C and D represent 1; and

(i) a unit of formula V wherein E represents an oxygen atom, E' represents a direct link, G represents a direct link, Ar represents a moiety of structure (iv), m and v represent zero, z represents 1, C and D represent 1;



Other second units which may form copolymers with any of said first repeat units (a) to (e) (and/or with units (aa), (bb) and (cc)) above include: a unit of formula IV wherein E and E' represent oxygen atoms, G represents a direct link, Ar represents a moiety of structure (v), m represents 0, w represents 1, s represents 0, A and B represent 1; or a unit of formula V wherein E and E' represent oxygen atoms, G represents a direct link, Ar represents a moiety of structure (v), m represents 0, z represents 1, v represents 0, C and D represent 1.

Preferred polymers for some situations may comprise first units selected from (a), (b), (c) and (e) and second units selected from (f), (g), (h) or (i). A polymer comprising units (d) and (h) may also be preferred. In some situations, first units may be selected from (aa), (bb) and (cc) and second units selected from (f), (g), (h) or (i).

More preferred polymers are copolymers having a first repeat unit selected from those described above, especially repeat units (b), (d) or (e) in combination with a second repeat unit selected from units (f) or (h). Other particularly preferred polymers are copolymers having a first repeat units selected from (aa) and (bb) in combination with a second repeat unit selected from units (f) or (h).

In some situations, a difficult to sulphonate unit may include at least one relatively strongly electron-withdrawing group (e.g. -CO- or -SO<sub>2</sub>- group) bonded to a phenyl group. Such a unit will be more difficult to sulphonate compared to, for example, a unit having a phenyl

group not bonded to such a strongly electron-withdrawing group. Thus, in this case, a copolymer comprising a unit (a) or (c) in combination with difficult to sulphonate units as described may be prepared. Preferred copolymers of this type may comprise first (difficult to sulphonate) repeat unit(s) of formula (b) and/or (d) together with second relatively easy to sulphonate) unit(s) of formula (a) and/or (c). Especially preferred copolymers comprise, preferably consist essentially of a first (difficult to sulphonate) repeat unit of formula (b) or (d) together with a second (relatively easy to sulphonate) unit of formula (a) or (c).

Preferred polymers having repeat unit(s) of formulae IV\* and V\* may include: a unit of formula IV\* wherein Ar represents a moiety of structure (v), E represents a direct link, E' represents an oxygen atom, G represents a direct link, w, s and m represent 0, A and B represent 1; and/or a repeat unit of formula V\* wherein Ar represents a moiety of structure (v), E represents a direct link, E' represents an oxygen atom, G represents a direct link, z, v and m represent 0, C and D represent 1.

Said polymers having repeat units IV\* and V\* may include any of repeat units (a) to (i) (and/or units (aa), (bb) and (cc)) described above.

In some situations, polymers which include at least one repeat unit of formula IV or formula IV\* may be preferred.

Copolymers may be prepared having one or more first repeat units and one or more of said second repeat units.

Said copolymers may be random or block copolymers.

Where said polymer is a copolymer as described, the mole% of co-monomer units, for example said first and  
5 second repeat units described above, may be varied to vary the solubility of the polymer in solvents, for example in solvents which may be used in the preparation of films and/or membranes from the polymers and/or in other solvents, especially water.

10

One class of first conductive polymers may comprise homopolymers, examples of which include sulphonated polyetheretherketone, polyetherketone,  
polyetherketoneketone, polyetheretherketoneketone,  
15 polyetherketoneetherketoneketone, polyetherdiphenylether ketone and polyethernaphthalene - ether - phenyl - ketone - phenyl..

Preferred polymers are substantially insoluble in  
20 boiling water.

First units of the type described above (with the exception of units (a) and (c)) may be relatively difficult to sulphonate, whereas second units of the type  
25 described may be easier to sulphonate.

Where a phenyl moiety is sulphonated, it may only be mono-sulphonated. However, in some situations it may be possible to effect bi- or multi-sulphonation.

30

In general terms, where a said polymer includes a -O-phenyl-O- moiety, up to 100 mole% of the phenyl moieties may be sulphonated. Where a said polymer includes a

-O-biphenylene-O- moiety, up to 100 mole% of the phenyl moieties may be sulphonated. It is believed to be possible to sulphonate relatively easily -O-(phenyl)<sub>n</sub>-O- moieties wherein n is an integer, suitably 1-3, at up to 100 mole%.  
5 Moieties of formula -O-(phenyl)<sub>n</sub>-CO- or -O-(phenyl)<sub>n</sub>-SO<sub>2</sub>- may also be sulphonated at up to 100 mole% but more vigorous conditions may be required. Moieties of formulae -CO-(phenyl)<sub>n</sub>-CO- and -SO<sub>2</sub>-(phenyl)<sub>n</sub>-SO<sub>2</sub>- are more difficult to sulphonate and may be sulphonated to a level less than  
10 100 mole% or not at all under some sulphonation conditions.

The glass transition temperature (T<sub>g</sub>) of said polymer may be at least 144°C, suitably at least 150°C, preferably at least 154°C, more preferably at least 160°C, especially  
15 at least 164°C. In some cases, the T<sub>g</sub> may be at least 170°C, or at least 190°C or greater than 250°C or even 300°C.

Said polymer may have an inherent viscosity (IV) of at  
20 least 0.1, suitably at least 0.3, preferably at least 0.4, more preferably at least 0.6, especially at least 0.7 (which corresponds to a reduced viscosity (RV) of least 0.8) wherein RV is measured at 25°C on a solution of the polymer in concentrated sulphuric acid of density 1.84gcm<sup>-3</sup>,  
25 said solution containing 1g of polymer per 100cm<sup>-3</sup> of solution. IV is measured at 25°C on a solution of polymer in concentrated sulphuric acid of density 1.84gcm<sup>3</sup>, said solution containing 0.1g of polymer per 100cm<sup>3</sup> of solution.

30 The measurements of both RV and IV both suitably employ a viscometer having a solvent flow time of approximately 2 minutes.

The main peak of the melting endotherm ( $T_m$ ) for said polymer (if crystalline) may be at least 300°C.

In general terms, said first conductive polymer is preferably substantially stable when used as a component of a PEM in a fuel cell. Thus, it suitably has high resistance to oxidation, reduction and hydrolysis and has very low permeability to reactants in the fuel cell. Preferably, however, it has a high proton conductivity. Furthermore, it suitably has high mechanical strength and is capable of being bonded to other components which make up a membrane electrode assembly.

Said polymer may comprise a film, suitably having a thickness of less than 1mm, preferably less than 0.5mm, more preferably less than 0.1mm, especially less than 0.05 mm. The film may have a thickness of at least 5 $\mu$ m.

Said polymer electrolyte membrane may comprise one or more layers wherein, suitably, at least one layer comprises a film of said polymer. Said membrane may have a thickness of at least 5 $\mu$ m and, suitably, less than 1mm, preferably less than 0.5mm, more preferably less than 0.1mm, especially less than 0.05mm.

25

It may be preferable for each phenyl group in a sulphonated polymer as described to be deactivated by being bonded directly to an electron withdrawing group, for example a sulphonated group, a sulphone group or a ketone group.

30

In one preferred embodiment, said first conductive polymer may include: polyaryletherketone and/or

polyarylethersulphone units; and units of formula  $-O-Ph_n-O-$  (XX) wherein Ph represents a phenyl group and n represents an integer of 2 or greater and wherein Ph groups of units (XX) are sulphonated.

5

Preferably, said first conductive polymer has at least some crystallinity or is crystallisable. The existence and/or extent of crystallinity in a polymer is preferably measured by wide angle X-ray diffraction, for example as described by Blundell and Osborn (Polymer 24, 953, 1983). Alternatively, crystallinity may be assessed by Differential Scanning Calorimetry (DSC).

Said first conductive polymer (especially when semi-crystalline) may have a solubility in NMP (at 25°C) of 4% or less.

Said first conductive polymer may have an EW (in g/mol) of less than 2000, suitably less than 1600, preferably less than 1200, more preferably less than 1000, especially less than 800. In some cases, the EW may be less than 600 or even less than 500. The ion-exchange capacity (IEC) (in meq/g) may be at least 0.3, suitably at least 0.5, preferably at least 0.8, more preferably at least 1.1, especially at least 1.5. In some cases, the IEC may be greater than 1.8, or even greater than 2.0.

Said polar protic solvent is preferably a component of a protic solvent formulation. Said protic solvent formulation preferably includes a major amount of said polar protic solvent.

In the context of this specification, a major amount suitably means that greater than 50 wt%, preferably greater than 70%, more preferably greater than 90 wt% or even 95 wt% of the referenced component is included in a formulation. Especially preferred is the case wherein the  
5 referenced component is present at about 100 wt%.

Said polar protic solvent may be selected from sulphuric acid, a sulphonic acid (e.g. methane sulphonic  
10 acid, trichloromethane sulphonic acid, trifluoromethane sulphonic acid), hydrofluoric acid and phosphoric acid. Said protic solvent formulation may include a mixture of components. Preferably, the sum of the wt% of polar  
protic solvents in said formulation represents a major  
15 amount of said formulation. The formulation may, nonetheless, include components which are not polar protic solvents.

Said protic solvent formulation may comprise at least  
20 90%, preferably at least 95%, more preferably at least 97%, especially at least 98% acid. An especially preferred polar protic solvent is sulphuric acid. Preferably, said protic solvent formulation includes at least 96%, preferably at least 98% acid. Said solvent may  
25 include less than 99% acid.

Said polar protic solvent (preferably also said protic solvent formulation) and said first conductive polymer may be selected so that said polar protic solvent (preferably  
30 also said formulation) does not functionalise said first conductive polymer to provide ion-exchange sites, for example sulphonate groups. Thus, in a preferred embodiment, said first conductive polymer includes easy to

5 sulphonate groups (as described above) which have already been sulphonated prior to contact with said polar protic solvent (or said formulation); and difficult to sulphonate groups which have not been sulphonated and which are not sulphonated by the polar protic solvent (or said protic solvent formulation) in the method.

10 Preferably, in the method, said first conductive polymer is solubilised, to some degree, on contact with said polar protic solvent (or by said protic solvent formulation if used). Preferably, said polar protic solvent (or said formulation) is capable of dissolving the first conductive polymer to a level of at least 5 wt%. Preferably, on contact with said polar protic solvent (or  
15 said formulation), the surface of said first conductive polymer is dissolved.

Said catalyst material may be any material which can act as a catalyst in an electrochemical device, for  
20 example a cell or which is a precursor of a material which may act as a catalyst. Said catalyst material preferably is in the form of finely divided electrically conductive particles. Said catalyst preferably comprises a catalytically active metal which may be selected from  
25 elements of groups VIIIa (preferably Fe, Co, Ni, Ru, Rh, Pd, Os, Ir, Pt), Ib (preferably Cu, Ag, Au), tin or titanium. Said catalyst may comprise an alloy or mixture, for example of more than one of said catalytically active metals; examples include combinations of  
30 platinum/ruthenium, platinum/ruthenium/tin; and iridium oxide/titanium. Said catalyst material may comprise a fine-grained powder of conductive carbon material, for example activated carbon, carbon black, graphite or



graphitised activated carbon, impregnated with catalytically active metal.

The surface coat weight of said catalyst material on  
5 said first conductive polymer is preferably at least 0.001 mg/cm<sup>2</sup> and preferably 10mg/cm<sup>2</sup> or less.

In the method of the first aspect, said catalyst material is preferably dispersed in said polar protic  
10 solvent and then the dispersion is contacted with said first material which comprises said first conductive polymer. At least 5 wt%, suitably at least 10 wt%, preferably at least 15 wt% of said catalyst material may be dispersed in said polar protic solvent (or said protic  
15 solvent formulation if used) contacted with said first ion-conducting polymer. The amount may be less than 30 wt%, preferably less than 25 wt%.

A second conductive polymer may be provided in, for  
20 example dissolved in, said polar protic solvent (or said protic solvent formulation if used). Said second conductive polymer may have any feature of said first conductive polymer described herein. Said first and second conductive polymers may be the same or different.  
25 Said second conductive polymer may be provided as a component of a blend comprising an ion-conducting polymer and non-ion-conducting polymer. Alternatively, a blend may comprise said second conductive polymer and a further conductive polymer (which may be as described in any  
30 statement herein).

Where a blend comprising a said ion-conducting polymer and a non-ion-conducting polymer (or polymers) are used the non-ion-conducting polymer(s) may be selected from:

- 5 - polymers which are resistant under the operating conditions of an electrochemical cell, are soluble in the same solvents (e.g. polar protic solvents) as the second conductive polymer and are suitable for improving the mechanical properties of the layer which incorporates the catalyst material, in particular soluble polymers, such as  
10 for example Ultrason S™ (aromatic polyether sulphone with bisphenol A units, from BASF AG), Ultrason E™ (aromatic polyether sulphone, from BASF AG), Radel™ (aromatic polyether sulphone with diphenylene units, from Amoco  
15 Performance Products) or Ultem™ (aromatic polyetherimide, from General Electric Co.),
- polymers which, by virtue of their hydrophobicity, are suitable for hydrophobising the surface of the layer which  
20 incorporates catalyst material, in particular fluoropolymers and PTFE. It is in particular expedient to provide only the side of the membrane electrode composite facing the cathode side (i.e. the "oxygen side") in use in a fuel cell with a hydrophobised outer layer, while a non-  
25 hydrophobised outer layer is applied onto the other side.
- semi-crystalline polymers having units I, II and/or III, for example semi-crystalline polymers selected from polymers described above which have a repeat unit of  
30 general formula IV, V, IV\* or V\*. Especially preferred examples of semi-crystalline polymers are polyetherketone, polyetheretherketone, polyetherketoneketone,

polyetheretherketoneketone and  
polyetherketoneetherketoneketone.

Said polar protic solvent (preferably also said protic  
5 solvent formulation if used) and said second conductive  
polymer may be selected so that said polar protic solvent  
(preferably also said formulation) does not functionalise  
the polymer to provide ion-exchange sites, for example  
sulphonate groups. Thus, in a preferred embodiment, said  
10 second conductive polymer includes easy to sulphonate  
groups (as described above) which have already been  
sulphonated prior to contact with said polar protic  
solvent (or said formulation); and difficult to sulphonate  
group which have not been sulphonated and which are not  
15 sulphonated by the polar protic solvent (or said protic  
solvent formulation) in the method. Alternatively, the  
polar protic solvent and the second conductive polymer may  
be such that the solvent cannot sulphonate the polymer.  
The use of methane sulphonic acid with sulphonated  
20 polyetheretherketone represents such a type.

Preferably, said second conductive polymer is caused  
to form a layer on said first conductive polymer.

25 Said layer may be at least  $1\mu\text{m}$  in thickness (after  
drying). The layer may have a thickness of less than 100  
 $\mu\text{m}$ .

After said catalyst material has been deposited on  
30 said first material, the polar protic solvent (or said  
protic solvent formulation) may be removed, for example  
caused to evaporate, and the composite formed may be  
dried. Preferably, however, the method includes the step

of increasing the porosity of the composite. In this regard, the method may include the step of contacting the composite, after catalyst material has been caused to deposit, with a second solvent. Said second solvent is preferably arranged to cause phase inversion of the material that it contacts. For example, where a second conductive polymer is provided as a layer on said first material, said second conductive polymer layer may be rendered porous, suitably by phase inversion. Thus, the method preferably includes the step of contacting said second conductive polymer layer with said second solvent.

Said second solvent (which may be used to cause phase inversion of said first or second conductive polymer) is preferably a non-solvent for the material (e.g. said first or second conductive polymer) that it is to cause phase inversion of. Preferred second solvents are aqueous; and examples include water and dilute acids.

After phase inversion the composite is preferably dried.

Said first conductive polymer preferably represents a major amount of said first material of said first aspect. Said first material may consist essentially of said first conductive polymer or said first material may be a composite which includes said first conductive polymer.

A composite membrane may be provided in a variety of ways. For example, an unsupported conductive polymer film can be preformed and laminated to the support material. Alternatively, (and preferably) the support material may be porous and a solution of the conductive polymer can be

impregnated into the support material. In one embodiment, the support material may comprise, or preferably consist essentially of, polytetrafluoroethylene, suitably provided as a porous film. Such a support material may be as  
5 described and used in accordance with the teachings of WO97/25369 and WO96/28242, the contents of which are incorporated herein by reference. Suitably, the support material has a porous microstructure of polymeric fibrils and is impregnated with said polymer throughout the  
10 material, preferably so as to render an interior volume of the membrane substantially occlusive.

Preferably, the method described above involves contacting a first surface of said first material with  
15 said polar protic solvent (or said protic solvent formulation) and deposition of said catalyst material over said first surface. The method may, additionally, include contacting a second surface of said first material with a polar protic solvent (or said protic solvent formulation)  
20 and depositing catalyst material on said second surface. . A membrane/electrode assembly having two electrodes may be defined after catalyst material has been deposited on said first and second surfaces. An electrode or electrodes of the assembly may be defined in a subsequent step after  
25 deposition of catalyst material. Alternatively, the electrode may be deposited with the catalyst material for example when carbon impregnated with platinum is used. The method of contacting said second surface may be as described in any statement herein. Advantageously, where a  
30 second conductive polymer is used as described above (it may be a "glue" which helps to fix the catalyst to the first conductive polymer) one type of second conductive polymer may be provided in the polar protic solvent

contacted with said first surface; and a different type of second conductive polymer may be provided in the polar protic solvent contacted with the second surface. Thus, the EW on opposite sides of the first material may be different.

A composite as described herein may be used in an electrochemical device, for example a fuel cell or electrolyser. A Membrane Electrode Assembly (MEA) preferably comprises or consists essentially of said membrane/electrode composite.

The invention extends to any novel composite as described herein per se.

The invention extends to a composite which includes a catalyst material on a first material wherein said composite is contaminated with a polar protic solvent, for example in an area adjacent said catalyst material. The contamination may comprise the residue of said polar protic solvent used to deposit the catalyst material, in a method according to said first aspect.

The invention extends to a method of preparing a MEA which includes associating an electrode with a composite as described herein.

The invention extends to any novel MEA described herein per se.

The invention extends to a MEA prepared using a method according to said first aspect and/or as described herein.

The invention extends to an electrochemical device, for example a fuel cell or electrolyser, incorporating a composite prepared in a method according to said first aspect and/or as described herein. The membrane may be  
 5 used in Hydrogen Fuel Cells or Direct Methanol Fuel Cells.

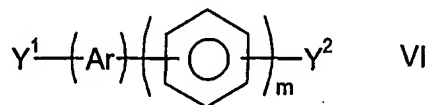
The following further utilities for the composite membrane are also contemplated:

- 10 1. Proton exchange membrane based water electrolysis, which involves a reverse chemical reaction to that employed in hydrogen/oxygen electrochemical fuel cells.
2. Chloralkali electrolysis, typically involving the electrolysis of a brine solution to produce chlorine  
 15 and sodium hydroxide, with hydrogen as a by-product.
3. Bipolar membranes employed in water splitting and subsequently in the recovery of acids and bases from waste water solutions.

20 Polymers having units I, II, III, IV, IV\*, V and/or V\* may be prepared by:

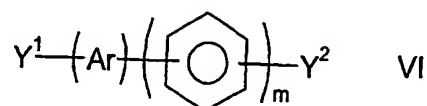
(a) polycondensing a compound of general formula

25

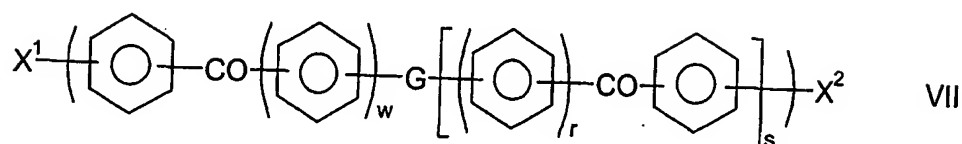


with itself wherein  $Y^1$  represents a halogen atom or a group -EH and  $Y^2$  represents a halogen atom or, if  $Y^1$   
 30 represents a halogen atom,  $Y^2$  represents a group E'H; or

(b) polycondensing a compound of general formula

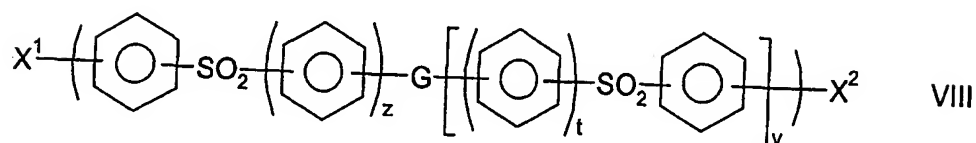


with a compound of formula



5

and/or with a compound of formula



10 wherein  $Y^1$  represents a halogen atom or a group -EH (or  
 -E'H if appropriate) and  $X^1$  represents the other one of a  
 halogen atom or group -EH (or -E'H if appropriate) and  $Y^2$   
 represents a halogen atom or a group -E'H and  $X^2$  represents  
 the other one of a halogen atom or a group -E'H (or -EH if  
 15 appropriate).

(c) optionally copolymerizing a product of a process as  
 described in paragraph (a) with a product of a process as  
 described in paragraph (b);

20



wherein the phenyl moieties of units VI, VII and/or VIII are optionally substituted; the compounds VI, VII and/or VIII are optionally sulphonated; and Ar, m, w, r, s, z, t, v, G, E and E' are as described above except that E  
5 and E' do not represent a direct link;

the process also optionally comprising sulphonating and/or cross-linking a product of the reaction described in paragraphs (a), (b) and/or (c) to prepare said polymer.

10

In some situations, the polymer prepared, more particularly phenyl groups thereof, may be optionally substituted with the groups hereinabove described after polymer formation.

15

Preferably, where  $Y^1$ ,  $Y^2$ ,  $X^1$  and/or  $X^2$  represent a halogen, especially a fluorine, atom, an activating group, especially a carbonyl or sulphone group, is arranged ortho- or para- to the halogen atom.

20

Preferred halogen atoms are fluorine and chlorine atoms, with fluorine atoms being especially preferred. Preferably, halogen atoms are arranged meta- or para- to activating groups, especially carbonyl groups.

25

Where the process described in paragraph (a) is carried out, preferably one of  $Y^1$  and  $Y^2$  represents a fluorine atom and the other represents an hydroxy group. More preferably in this case,  $Y^1$  represents a fluorine atom and  $Y^2$   
30 represents an hydroxy group. Advantageously, the process described in paragraph (a) may be used when Ar represents a moiety of structure (i) and m represents 1.

When a process described in paragraph (b) is carried out, preferably,  $Y^1$  and  $Y^2$  each represent an hydroxy group. Preferably,  $X^1$  and  $X^2$  each represent a halogen atom, suitably the same halogen atom.

5

Any feature of any aspect of any invention or embodiment described herein may be combined with any feature of any aspect of any other invention or embodiment described herein.

10

Specific embodiments of the invention will now be described, by way of example, with reference to Figure 1 which is a schematic representation of a polymer electrolyte membrane fuel cell; and to Figure 2 which shows various first conductive polymers.

15

Unless otherwise stated, all chemicals referred to hereinafter were used as received from Sigma-Aldrich Chemical Company, Dorset, U.K.

20

Examples 1 and 2 describe the preparation of polymers which can be sulphonated as described in Example 3. Example 4 describes how a conductive membrane may be prepared from the polymer of Example 1 (after sulphonation as described in Example 3) and Examples 5 and 6 describe how the membrane of Example 4 may be coated with a catalyst using a "glue" to adhere the catalyst to the membrane. The glue comprises the polymer of Example 1 (after sulphonation as described in Example 3) in Example 5 and the polymer of Example 2 (after sulphonation as described in Example 4) in Example 6.

25  
30

Example 1

A 700ml flanged flask fitted with a ground glass Quickfit lid, stirrer/stirrer guide, nitrogen inlet and  
5 outlet was charged with 4,4'-difluorobenzophenone (89.03g, 0.408 mole), 4,4'-dihydroxybiphenyl (18.62g, 0.10 mole) 4,4'-dihydroxydiphenylsulphone (75.08g, 0.30 mole), and diphenysulphone (332g) and purged with nitrogen for over 1 hour. The contents were then heated under a nitrogen  
10 blanket to between 140 and 150°C to form an almost colourless solution. While maintaining a nitrogen blanket, dried sodium carbonate (43.24g, 0.408 mole) was added. The temperature was raised gradually to 315°C over 3 hours then maintained for 0.5 hours.

15

The reaction mixture was allowed to cool, milled and washed with acetone and water. The resulting polymer was dried in an air oven at 120°C. The polymer had a melt viscosity at 400°C, 1000sec<sup>-1</sup> of 0.72 kNsm<sup>-2</sup>.

20

Example 2

A 700ml flanged flask fitted with a ground glass Quickfit lid, stirrer/stirrer guide, nitrogen inlet and  
25 outlet was charged with 4,4'-difluorobenzophenone (89.03g, 0.408 mole), 4,4'-dihydroxybiphenyl (37.24g, 0.20 mole) 4,4'-dihydroxybenzophenone (42.84g, 0.20 mole), and diphenysulphone (332g) and purged with nitrogen for over 1 hour. The contents were then heated under a nitrogen  
30 blanket to between 140 and 150°C to form an almost colourless solution. While maintaining a nitrogen blanket, dried sodium carbonate (43.24g, 0.408 mole) was

added. The temperature was raised gradually to 315°C over 2 hours then maintained for 1 hours.

The reaction mixture was allowed to cool, milled and washed with acetone and water. The resulting polymer was dried in an air oven at 120°C. The polymer had a melt viscosity at 400°C, 1000sec<sup>-1</sup> of 0.48 kNsm<sup>-2</sup>.

#### Example 3 - General Procedure for sulphonation of polymers

The polymer of Examples 1 and 2 were sulphonated by stirring each polymer in 98% sulphuric acid (3.84g polymer/100g sulphuric acid) for 21 hours at 50°C. Thereafter, the reaction solution was allowed to drip into stirred deionised water. Sulphonated polymer precipitated as free-flowing beads. Recovery was by filtration, followed by washing with deionised water until the pH was neutral and subsequent drying. In general, titration confirmed that 100 mole% of the biphenyl units had sulphonated, giving one sulphonic acid group, ortho to the ether linkage, on each of the two aromatic rings comprising the biphenyl unit.

#### Example 4 - Membrane Fabrication

Membranes were produced from the polymer from Example 1 (after sulphonation as described in Example 3) by dissolving the polymer in N-methylpyrrolidone (NMP). The polymer was dissolved at a concentration of 15% w/w. The homogeneous solution was cast onto clean glass plates and then drawn down to give 600 micron films, using a stainless steel Gardner Knife. Evaporation at 100°C under

vacuum for 24 hours produced membranes of mean thickness 60 microns.

5     Example 5 - Coating of Membrane from Example 4 with catalyst

10     A catalyst dispersion was prepared by dissolving the sulphonated polymer from Example 1 (0.70g) in 98% sulphuric acid (5.54ml) and adding carbon impregnated with platinum (20% w/w) (0.53g). The mixture was stirred vigorously, cast onto one surface of the membrane prepared as described in Example 4, drawn down using a stainless steel Gardner Knife. The membrane was immersed in deionized water, removed, dried under vacuum at 105°C. The  
15     casting procedure was repeated on the other surface of the membrane, thereby producing a microporous catalyst surface on both sides of the membrane.

20     Example 6 - Coating of Membrane from Example 4 with catalyst

25     A catalyst dispersion was prepared by dissolving the sulphonated polymer from Example 2 (0.70g) in 98% sulphuric acid (5.54ml) and adding carbon impregnated with platinum (20% w/w) (0.53g). The mixture was stirred vigorously, cast onto a membrane prepared as described in Example 4, drawn down using a stainless steel Gardner Knife. The membrane was immersed in deionized water, removed, dried under vacuum at 105°C. The casting  
30     procedure was repeated on the other surface of the membrane, thereby producing a microporous catalyst surface on both sides of the membrane.

The reader's attention is directed to all papers and documents which are filed concurrently with or previous to this specification in connection with this application and which are open to public inspection with this  
5 specification, and the contents of all such papers and documents are incorporated herein by reference.

All of the features disclosed in this specification (including any accompanying claims, abstract and  
10 drawings), and/or all of the steps of any method or process so disclosed, may be combined in any combination, except combinations where at least some of such features and/or steps are mutually exclusive.

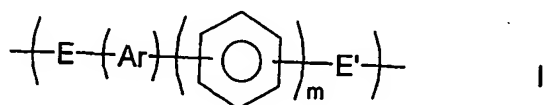
15 Each feature disclosed in this specification (including any accompanying claims, abstract and drawings), may be replaced by alternative features serving the same, equivalent or similar purpose, unless expressly stated otherwise. Thus, unless expressly stated otherwise,  
20 each feature disclosed is one example only of a generic series of equivalent or similar features.

The invention is not restricted to the details of the foregoing embodiment(s). The invention extend to any novel  
25 one, or any novel combination, of the features disclosed in this specification (including any accompanying claims, abstract and drawings), or to any novel one, or any novel combination, of the steps of any method or process so disclosed.

CLAIMS

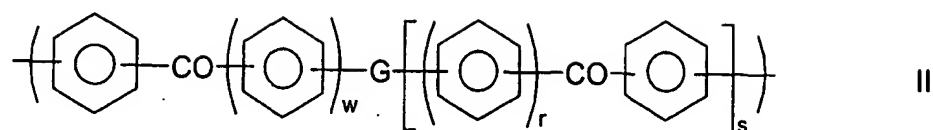
1. A method of manufacturing a composite of a type which includes a catalyst material on a first material which  
5 comprises a first conductive polymer, the method including the step of contacting said first material comprising said first conductive polymer with a polar protic solvent and causing catalyst material to deposit on said first material.
- 10 2. A method according to Claim 1, wherein said polar protic solvent is a component of a protic solvent formulation wherein said first material is contacted with said protic solvent formulation.
- 15 3. A method according to Claim 1 or Claim 2, wherein said polar protic solvent is selected from sulphuric acid, a sulphonic acid, hydrofluoric acid and phosphoric acid.
- 20 4. A method according to any preceding claim, wherein said polar protic solvent does not functionalise said first conductive polymer to provide ion-exchange sites on contact therewith.
- 25 5. A method according to any of Claims 2 to 4, wherein said first conductive polymer is solubilised on contact with said protic solvent formulation.
- 30 6. A method according to any preceding claim, wherein said catalyst material is dispersed in said polar protic solvent and/or said protic solvent formulation and the dispersion is contacted with said first material.

7. A method according to any preceding claim, wherein a second conductive polymer is provided in said polar protic solvent and/or said protic solvent formulation.
- 5 8. A method according to Claim 7, wherein said polar protic solvent does not functionalise said second conductive polymer to provide ion-exchange sites.
9. A method according to any preceding claim, the method  
10 including the step of contacting the composite after catalyst material has been caused to deposit with a second solvent to increase the porosity of the composite.
10. A method according to any preceding claim, wherein  
15 said first conductive polymer comprises a thermoplastic or thermoset aromatic polymer, a polybenzazole or a polyaramid polymer, or a perfluorinated ionomer, each of which has been functionalised to provide ion-exchange sites; polystyrene sulphonic acid, polytrifluorostyrene  
20 sulphonic acid, polyvinyl phosphonic acid, polyvinyl carboxylic acid and polyvinyl sulphonic acid polymers, and metal salts thereof.
11. A method according to any preceding claim, wherein  
25 said first conductive polymer is one having a moiety of formula

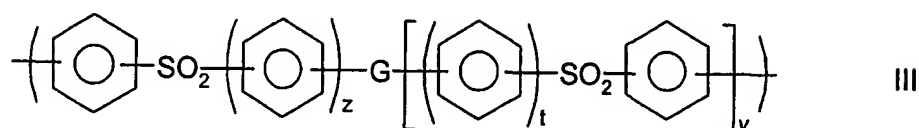


and/or a moiety of formula





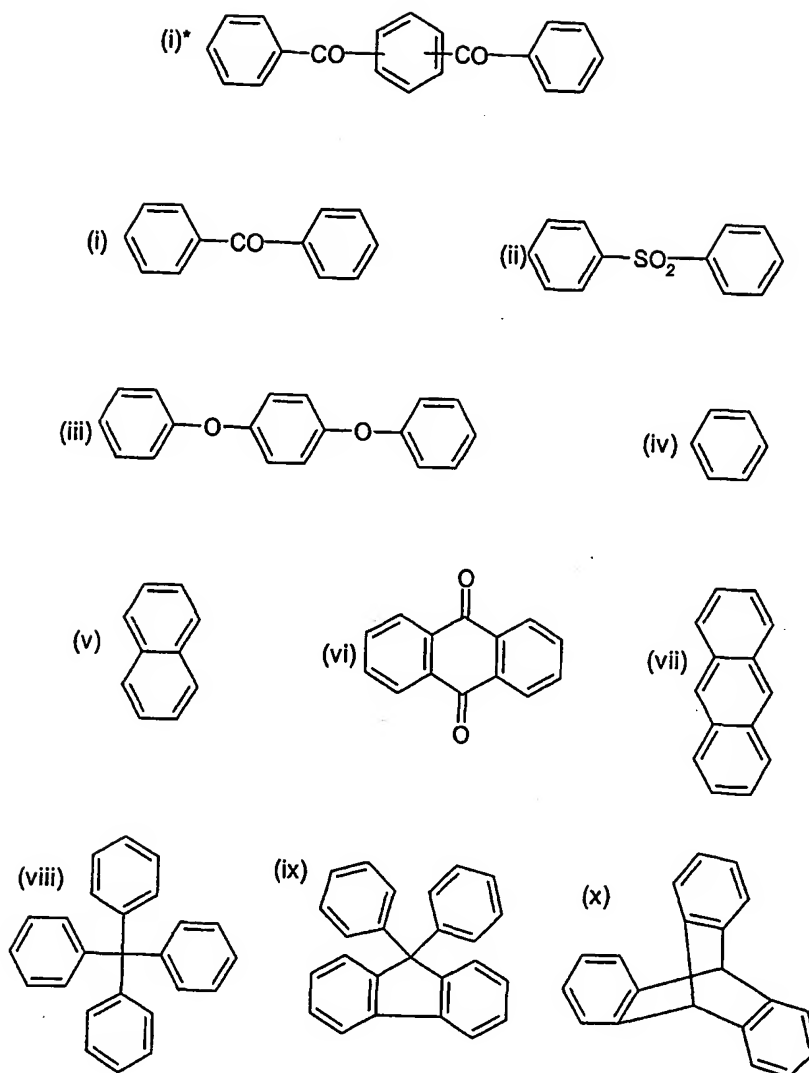
and/or a moiety of formula



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wherein at least some of the units I, II and/or III are  
 funtionalized to provide ion-exchange sites; wherein the  
 phenyl moieties in units I, II, and III are independently  
 10 optionally substituted and optionally cross-linked; and  
 wherein m,r,s,t,v,w and z independently represent zero or a  
 positive integer, E and E' independently represent an  
 oxygen or a sulphur atom or a direct link, G represents an  
 oxygen or sulphur atom, a direct link or a -O-Ph-O- moiety  
 15 where Ph represents a phenyl group and Ar is selected from  
 one of the following moieties (i)\* or (i) to (x) which is  
 bonded via one or more of its phenyl moieties to adjacent  
 moieties

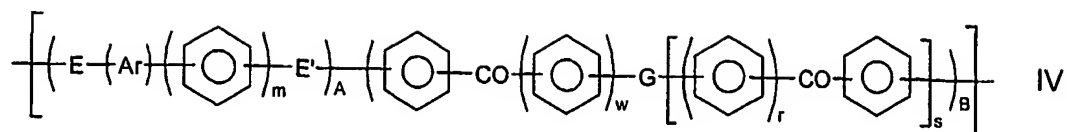
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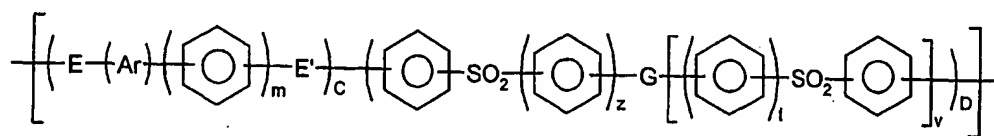
12. A method according to any preceding claim, wherein said first conductive material is sulphonated.

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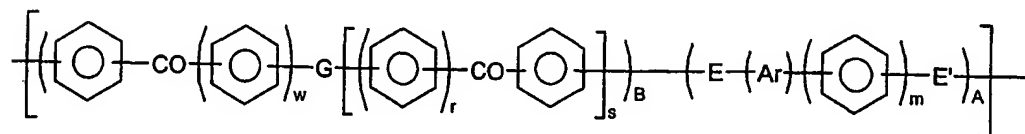
13. A method according to any preceding claim, wherein said first conductive polymer is a homopolymer having a repeat unit of general formula



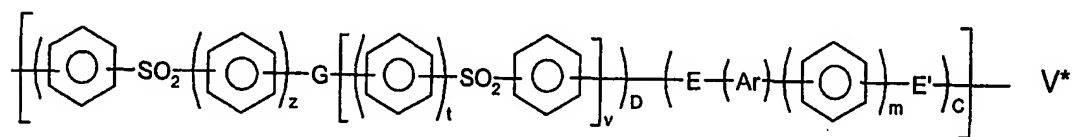
or a homopolymer having a repeat unit of general formula



5 or a homopolymer having a repeat unit of general formula



or a homopolymer having a repeat unit of general formula



10 or a random or block copolymer of at least two different units selected from IV and V or from IV\* and V\*,

wherein A, B, C and D independently represent 0 or 1 and E, E', G, Ar, M, r, s, t, v, w and z are as described in  
15 claim 11.

14. A method according to any preceding claim, wherein said first conductive polymer includes at least some ketone moieties in the polymeric chain.
- 5 15. A method according to any preceding claim, wherein said first conductive polymer includes a multi-phenylene moiety or a fused ring aromatic moiety.
- 10 16. A method according to claim 15, wherein a said multi-phenylene moiety or fused ring aromatic moiety is bonded to two oxygen atoms.
- 15 17. A method according to any preceding claim, wherein said first conductive polymer includes a -O-biphenylene-O- or -O-naphthalene-O- moiety.
18. A method according to any preceding claim, wherein said first conductive polymer is a copolymer comprising a first repeat unit selected from the following:
- 20
- (a) a unit of formula IV wherein E and E' represent oxygen atoms, G represents a direct link, Ar represents a moiety of structure (iv), m and s represent zero, w represents 1 and A and B represent 1;
- 25
- (b) a unit of formula IV wherein E represents an oxygen atom, E' represents a direct link, Ar represents a moiety of structure (i), m represents zero, A represents 1, B represents zero;
- 30
- (c) a unit of formula V wherein E and E' represent oxygen atoms, G represents a direct link, Ar represents a

moiety of structure (iv), m and v represent zero, z represents 1 and C and D represent 1;

(d) a unit of formula V wherein E represents an oxygen atom, E' represents a direct link, Ar represents a moiety of structure (ii), m represents 0, C represents 1, D represents 0; or

(e) a unit of formula V wherein E and E' represents an oxygen atom, Ar represents a structure (i), m represents 0, C represents 1, Z represents 1, G represents a direct link, v represents 0 and D represents 1;

(aa) a unit of formula IV wherein E represents an oxygen atom, E' represents a direct link, Ar represents a structure (i)\*, m represents 0, A represents 1, B represents 0;

(bb) a unit of formula IV wherein E and E' represent oxygen atoms, Ar represents a structure (iv), m and w represent 0, G represents a direct link, s and r represent 1, A and B represent 1;

(cc) a unit of formula IV wherein E and E' represent oxygen atoms, Ar represents a structure (i), m and w represent 0, G represents a direct link, s and r represent 1, A and B represent 1;

and a second repeat unit which is selected from the following:

(f) a unit of formula IV wherein E and E' represent oxygen atoms, G represents a direct link, Ar represents a

moiety of structure (iv), m represents 1, w represents 1, s represents zero, A and B represent 1;

(g) a unit of formula IV wherein E represents an oxygen atom, E' is a direct link, G represents a direct link, Ar represents a moiety of structure (iv), m and s represent zero, w represent 1, A and B represent 1;

(h) a unit of formula V wherein E and E' represent oxygen atoms, G represents a direct link, Ar represents a moiety of structure (iv), m represents 1, z represents 1, v represents 0, C and D represent 1; and

(i) a unit of formula V wherein E represents an oxygen atom, E' represents a direct link, G represents a direct link, Ar represents a moiety of structure (iv), m and v represent zero, z represents 1, C and D represent 1;

(j) a unit of formula IV wherein E and E' represent oxygen atoms, G represents a direct link, Ar represents a moiety of structure (v), m represents 0, w represents 1, s represents 0, A and B represent 1;

(k) a unit of formula V wherein E and E' represent oxygen atoms, G represents a direct link, Ar represents a moiety of structure (v), m represents 0, z represents 1, v represents 0, C and D represent 1.

19. A method according to any of claims 1 to 14, wherein said first conductive polymer comprises a copolymer comprising a unit (a) and/or (c) as described in claim 18 in combination with a unit (b), (d), (e), (aa), (bb) and/or (cc) as described in claim 18.

20. A method according to any preceding claim, wherein the composite is for use in an electrochemical device.

21. A composite which includes a catalyst material on a  
5 first material wherein said composite is contaminated with  
a polar protic solvent.

22. A method of preparing a membrane electrode assembly  
which includes associating an electrode with a composite  
10 prepared in a method according to any of Claims 1 to 20.

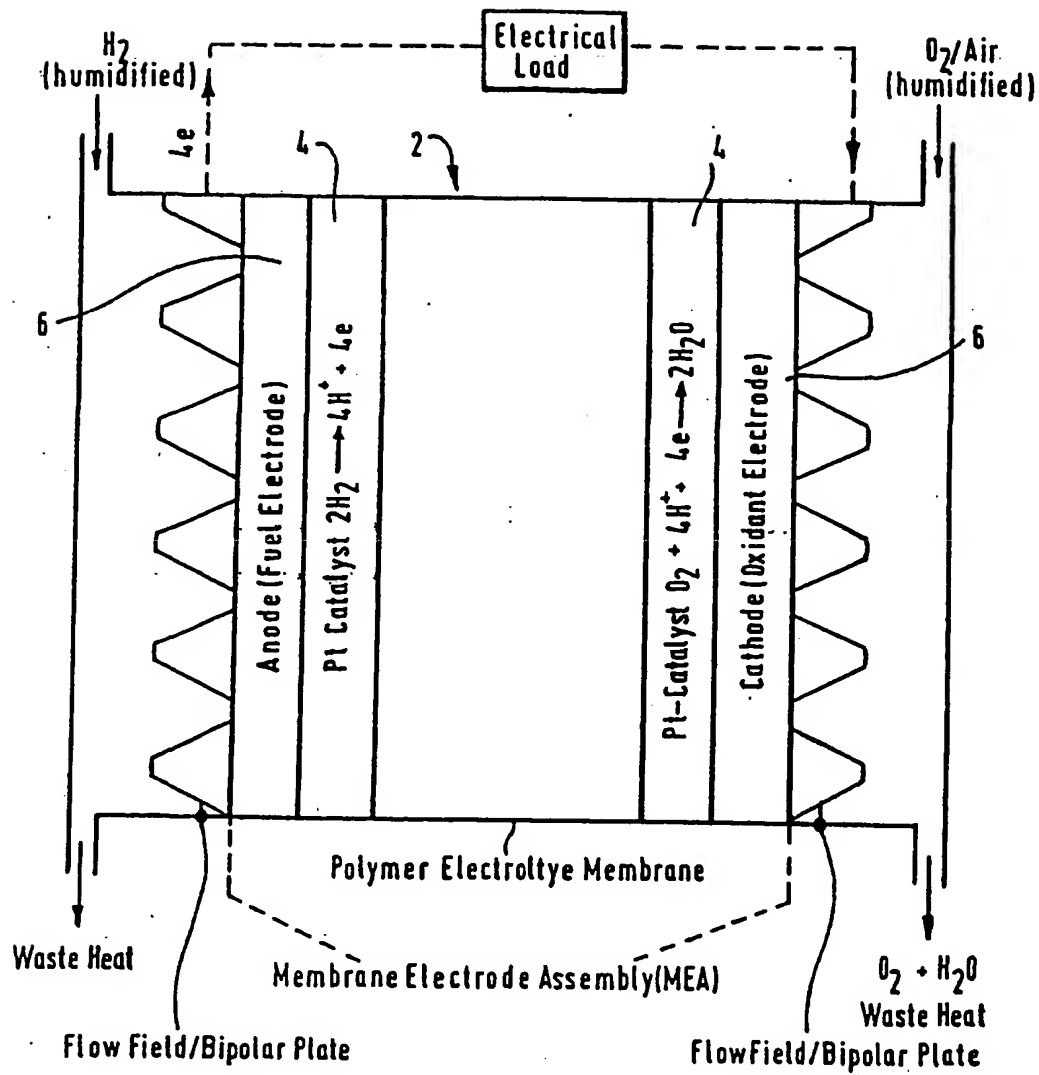


Figure 1



PEI (polyetherimide) R=aryl, alkyl, aryl ether or alkylether	
Udel polysulfone	
Radel R polyphenylsulfone	
Radel A polyethersulfone	
poly(trifluoro-methyl- bis(phthalimide)-phenylene)	
poly(triphenylphosphine oxide sulfide-phenylsulfone-sulfide)	
(PBO-PI) poly(benz(bis)oxazole)	
poly(phenylsulfide 1,4- phenylene)	

Figure 2a

poly(trifluoromethyl-bis(phthalimide)-phenylsulfone)	
(PVSA) polyvinyl sulfonic acid	
poly(phthalimide ditrifluoromethyl methylene phthalimide-1,3-phenylene ether)	
poly-x (maxdem)	
poly(pyromellitic diimide-1,3-phenylene)	
poly(diphthalimide-1,3-phenylene)	
(PPO) poly(1,4-phenylene oxide)	
Diphenyl PPO (poly(3,5-diphenyl-1,4-phenylene oxide))	
PBPS (poly(benzophenone sulfide))	

Figure 2b

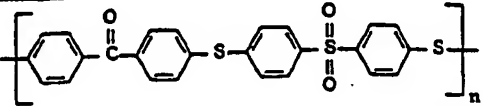
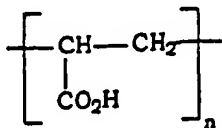
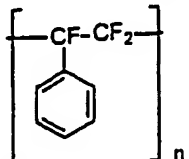
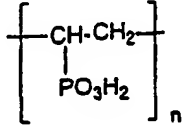
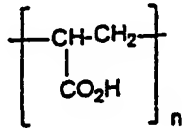
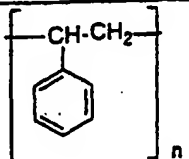
poly(benzophenone sulfide-phenylsulfone-sulfide)	
polyvinyl carboxylic acid	
trifluoro styrene	
polyvinyl phosphonic acid	
polyvinyl carboxylic acid	
polystyrene sulfonic acid (PSSA)	

Figure 2c

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